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The Temperature Coefficient of the Weight of a Falling Drop as a Means of Estimating the Molecular Weight and the Critical Temperature of a Liquid.

DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE FACULTY OF PURE SCIENCE IN COLUMBIA UNIVERSITY IN THE CITY OF NEW YORK.

BY

ERIC HIGGINS
NEW YORK CITY

1908

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This work was carried out under the direction of Professor J. Livingston Rutgers Morgan at his suggestion. The author begs to tender his sincere thanks for the assistance, advice and encouragement accorded to him during the course of the work by Professor Morgan. E. H.

The Temperature Coefficient of the Weight of a Falling Drop as a Means of Estimating the Molecular Weight and the Critical Temperature of a Liquid.

Object of the Investigation.

In a recent paper,[1] it was shown that the weight of a drop of liquid falling from a properly constructed tip is proportional for any one diameter of tip, to the surface tension of the liquid; and, further, that when falling drop weights are substituted for surface tensions as measured by capillary rise in the formula of Eötvös, as modified and presented in two forms by Ramsay and Shields, the molecular weights and critical temperatures of liquids can be calculated with an accuracy equal to that attained by the use of the surface tensions found from the capillary rise.

The object of the present work was to measure the magnitude of falling drop weights with the utmost possible accuracy and thus to test the conclusions of Morgan and Stevenson; to determine if irregularities in the constant value (K_{temp}) were real or due to experimental error and to conclusively establish the relative value of this method of determination of the molecular weight and critical temperature as compared with other methods for arriving at these values. The results of my work, it may be said here, have not only confirmed the conclusions of Morgan and Stevenson in every respect, as far as concerns any one tip, but in addition have shown

[1] Morgan and Stevenson, J. A. C. S., 30, 360–376, 1908.

that for the determination of relative surface tensions, the drop method is more accurate than the one in common use, which depends upon capillary rise. Further, they show that the molecular temperature coefficient of drop weight $K_{(temp.)}$ is really a constant, although Ramsay and Shields, for the same liquids, found the corresponding molecular temperature coefficient of surface tension (k), from capillary rise, to vary so much that for the calculation of critical temperatures it was necessary to first find the exact value of k for the liquid in question. This is not necessary when working with drop weights, the one constant value, holding for all the non-associated liquids studied, and so presumably for all the others.[2] This apparently also makes the drop-weight method at its best, more accurate as a means of determining the molecular weight than any other method, with the exception of that for permanent gases, which is based upon the density.

Apparatus and Method.

The apparatus for the measurement of the volume of a single falling drop (Figure 1) in construction was essentially the same as that employed by Morgan and Stevenson, differing only in having a more accurate capillary burette (1 mm. corresponding to 0.000,046 cc.) and in having the tip joined directly to it, without the interposition of a wider tube. My burette was also of greater length (2.5 meters) thus allowing drops of the liquids having the highest drop volumes to be measured without the use of the bulbs, which were found to be a danger when using the more viscous liquids, owing to drainage difficulties. The smaller diameter of the burette enabled me to obtain more accurate readings, the uniformity of the tube removed difficulties as to drainage, and the absence of a constricted "zero mark" permitted a more deliberate and accurate reading. To obviate the possible loss of a reading due to the meniscus falling in a bend of the burette tube or at the place where the joining

[2] See second part.

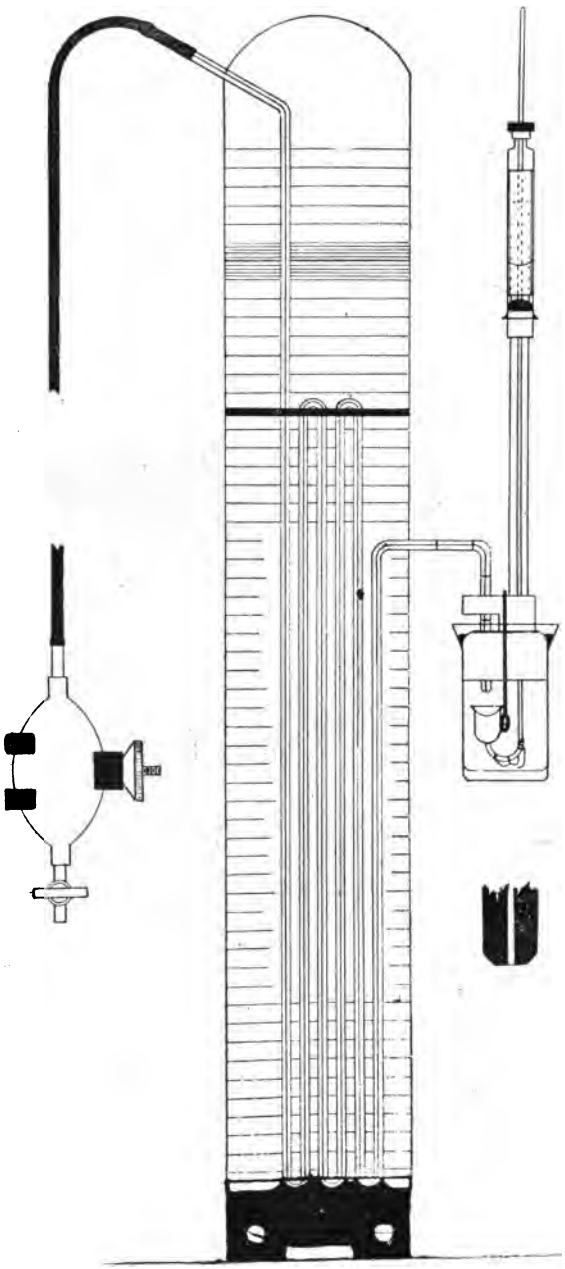

FIG. 1.

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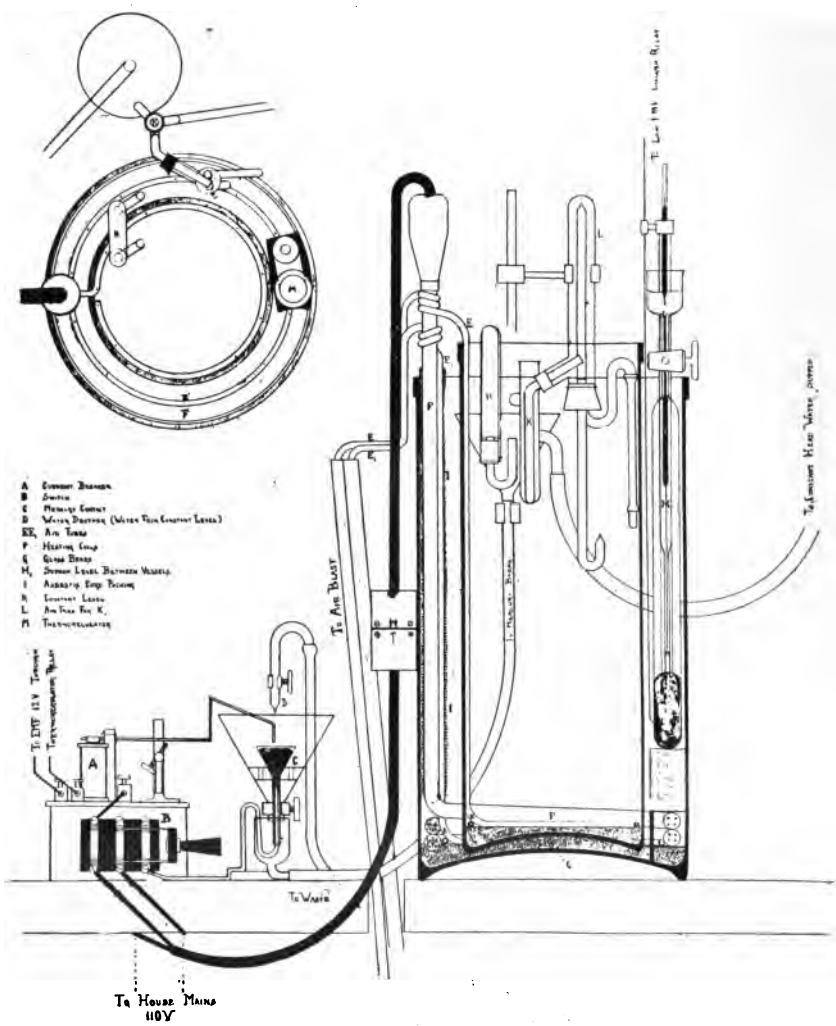


FIG. 2.

of the two lengths of capillary tubing composing it had distorted the bore, four "zero marks" at successive distances of one centimeter from one another were scratched upon the burette tubing just above the tip and the exact relative volumes of the intervals between them determined. In all other respects the apparatus was exactly the same as that employed by Morgan and Stevenson and was operated in the same way.

The dimensions of the apparatus, 69 × 18 centimeters, introduced difficulties in maintaining a constant and uniform temperature. The electrically heated thermostat finally adopted for the purpose is shown in Figure 2, and the electrical connections diagrammatically in Figure 3. The heating coil and thermo-regulator placed in the outer vessel (a 60 × 30 centimeter glass anatomical jar) maintained the inner cylinder (another jar, 60 × 20 centimeters) in a bath, the temperature of which varied rapidly within narrow limits. The variation of temperature in the inner vessel was naturally much smaller than this, and it was found easily possible to retain it constant at any temperature, from 24° to 76° within 0.02° for any desired length of time. I believe that this "jacket" system yields the most satisfactory results where the conditions limit the disposition of the heating arrangements, and large instruments are to be dealt with. The vibration of mechanical stirrers being fatal to the accurate determination of drop volumes, the water in both the inner and outer cylinders was thoroughly agitated by a current of air passing through block-tin pipes. The trouble which might be caused by the breaking down of the syphon constant level, owing to the liberation of dissolved air from the cold feed water, was obviated by the air trap shown in the figure.

The heating current being heavy (10 to 20 amperes at 110 volts) was found to be best broken from a surface of mercury beneath water continually supplied from the overflow of the constant level. The current breaker was operated by twelve "gravity" cells thrown in through a small relay

operated through the toluol thermo-regulator by two of the same cells. By thus breaking a very weak current in the regulator no trouble was experienced from the contamination of its mercury surface. The apparatus in this form ran continuously at various temperatures and without attention or cleaning for six months and gave perfectly satisfactory results, the only trouble lying in the impossibility of obtaining glass vessels of this size which were sufficiently well annealed to support the higher temperatures for more than six or eight weeks, as is evidenced by the fact that I was forced to replace these three times during the course of the work.

The capillary burette was calibrated with mercury at 20°, successive quantities being blown out and weighed, the operation being repeated four times. The summated volumes calculated from these weights differed from that calculated from the weight of the total content (0.1230 cubic centimeter) by only 0.000,003 cubic centimeter. This calibration was further checked by measuring the length of various threads of mercury in all parts of the tube, thus measuring each centimeter of the burette. These results were plotted on a curve from which volumes could be read to 0.000,005 cubic centimeter. In the calibration in air the position of the meniscus was read through an uncorrected lens, taking advantage of its lack of rectilinearity to avoid parallax. In the estimations in the thermostat the same object was attained when taking an observation of the "zero marks" by the use of narrow slits in a mask attached to the outer cylinder centering on similar slits on the opposite side, from which the necessary illumination was obtained from a small electric lamp. The measuring tube itself, when in the thermostat, acted like an uncorrected lens in making readings of the values on the graduated scale.

This calibration being performed at 20°, it was necessary to determine the effect of temperature in dilating the tube and expanding the scale. The volume of a thread of mercury, as given by the curve, was observed at every 10°, between

DIAGRAM OF ELECTRIC CONNECTIONS

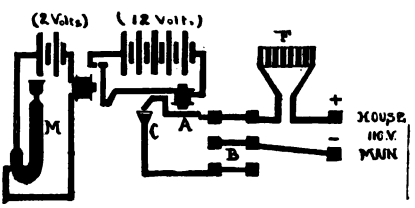


FIG. 3.

5° and 85°, the mercury being subsequently weighed and its true volume calculated at each of the temperatures. This work showed the effect of dilation to be very small, amounting to but 0.000,000,14 cubic centimeter per centimeter of length per degree. All volumes read were corrected in accord with this. The possibility of a residual dilation effect on the capillary tube after heating to high temperatures was guarded against by working alternately on an ascending and descending thermometer. A series of estimations at one temperature occupying at least a day, the passage from low to high, and again to low temperature extended over periods of from six to ten days, thus reducing to a minimum the effect of residual dilation.

As a further check on the accuracy of our original calibration and of our assumption of the absence of residual dilation, the total content of the burette was measured three times during the course of the work and no appreciable difference observed.

As mentioned by Morgan and Stevenson, all difficulties occasioned by condensation on, or evaporation from, the drop when forming is prevented by the production of a "fog" upon the walls of the dropping cup. This condition I find to be most readily induced by dusting fine graphite powder upon the walls of the cup above the liquid. By then heating the liquid to a temperature of 100° (or as near that as possible without causing it to boil) for five minutes and plunging the cup in cold water, vapor is deposited upon the various particles, producing a satisfactory and durable fog. The instrument is then placed in the thermostat and a drop allowed to hang from the tip for an hour. At the end of this time the conditions are such that a drop neither gains nor loses in volume. Before each measurement I assured myself, by drawing the drop back into the burette several times, that such a condition prevailed, and that the drop neither gained nor lost in volume. When passing from one temperature to another the fog can be maintained by allowing a drop to hang from the tip during the change.

Since a thermometer could not very well be placed in the dropping cup itself a similar cup containing a fog was placed beside the burette, a certified thermometer taking the place of the tip and no estimation was made until the thermometer within the "blank" had agreed with a similar thermometer within the thermostat for a half hour. Without this somewhat elaborate procedure it was impossible to get agreeing results, drop weight being very sensitive to changes in temperature.

To prove that drainage difficulties were absent, a short thread of liquid was drawn through the tube at various speeds, from one centimeter to one millimeter per second, and the length of the thread measured after each passage, but so long as the walls of the capillary were wetted no alteration in volume could be detected with any of the six liquids used.

Morgan and Stevenson measured the volume of a single drop, for it seemed from the work of other investigators that the successive formation of several drops might introduce complications. My work has shown that, in the presence of a perfect fog and constant temperature, a succession of drops (*i. e.*, where the clinging drop remaining after each fall is not drawn back in the burette, but is again increased to the falling point, and simply one final reading made) gives a mean value for one drop that is exactly concordant with that obtained from the measurement of a single drop. Naturally, here, the greatest speed of formation of the drop is somewhat over a minute, owing to the small diameter of the burette.

Results.

My results, in detail, for the same liquids used by Morgan and Stevenson, and also for carbon tetrachloride, are given in Tables I to VI. All my densities were carefully redetermined with a 25 cubic centimeters Ostwald pyknometer, and agreed in the main with those collected from various sources by Rénard and Guye. With quinoline, only, was the variation worth considering, and even that did not change

appreciably the values of the surface tension as given by Rénard and Guye. The chemicals used were the purest obtainable. The aniline, pyridine, benzene and chlorbenzene were Kahlbaum's "Special K," the carbon tetrachloride, Baker's "Analyzed" and the quinoline Merck's "Pure synthetical;" and all showed the correct and constant boiling-points.

In the first column of Tables I–VI is given the temperature; the second contains the actually determined drop volumes, all from the same beveled tip, approximately 6 millimeters in diameter; the third the average drop volume and its mean error, assuming no constant error to exist; the fourth the density; the fifth the drop weight, the product of the average drop volume and the density; the sixth the value

$$K_{temp.} = \frac{w_1\left(\frac{M}{d_1}\right)^{\frac{1}{3}} - w_2\left(\frac{M}{d_2}\right)^{\frac{1}{3}}}{T_2 - T_1},$$

w_1 and w_2 being drop weights in milligrams at the temperatures t_1 and t_2, and d_1 and d_2 the densities, while M is the molecular weight. And, finally, the seventh column in three of the tables contains the value

$$K = \frac{\gamma_1\left(\frac{M}{d_1}\right)^{\frac{1}{3}} - \gamma_2\left(\frac{M}{d_2}\right)^{\frac{1}{3}}}{T_2 - T_1}$$

as calculated from Rénard and Guye's surface tensions (γ_1 and γ_2) from capillary rise in saturated air. These are given where four or more temperatures are employed to show the relative variation of the values of $K_{temp.}$ and of Rénard and Guye's k, as found for the six liquids, together with the critical temperatures as observed and as calculated from $K_{temp.}$ and k, by aid of the formulas

$$w\left(\frac{M}{d}\right)^{\frac{1}{3}} = K_{temp.}(\tau - 6)$$

and

$$\gamma\left(\frac{M}{d}\right)^{\frac{1}{3}} = k(\tau - 6),$$

where τ is the difference between the critical temperature and that of observation. Here I have used for $K_{temp.}$ in all cases the actually obtained results most separated as to temperature, and not those from a smoothed curve, as is done for the k values, and has been done by all investigators using the capillary rise method.

In Figure 4 the comparative accuracy of drop weights and the surface tensions by capillary rise for the liquids which were studied at three or more temperatures, is also shown graphically, the surface tensions being the very carefully determined ones of Rénard and Guye against saturated air. It must be noted here that the graphs are only to be compared in relative straightness and NOT AS TO SLOPE, for I have as yet made no attempt to express drop weights accurately in terms of surface tension.

It will be noted that my two intermediate results for pyridine lie somewhat off the curve, one on either side, although the low and the high values lead to the satisfactory result for $K_{temp.}$ shown in Table VII. These errors are probably due to slight temperature errors, for pyridine was the first liquid investigated, and our first method for the agitation of the water in the inner cylinder was found later to be insufficient. This difficulty was avoided at both the low and the high temperatures, these determinations having been made subsequently.

TABLE I.

BENZENE.

Temp.	Drop volume, cc.	Mean volume, cc.	Density.	Drop weight, mmg.	$K_{temp.}$	$k_{R \& G.}$
11.4	0.039680 0.039692 0.039674 0.039686	0.039683 ±0.000.003 or 0.01%	0.888	35.239	2.521	1.717
30.2	0.037252 0.037285 0.037274 0.037269	0.03727 ±0.000.007 or 0.02%	0.868	32.350	2.583	2.230

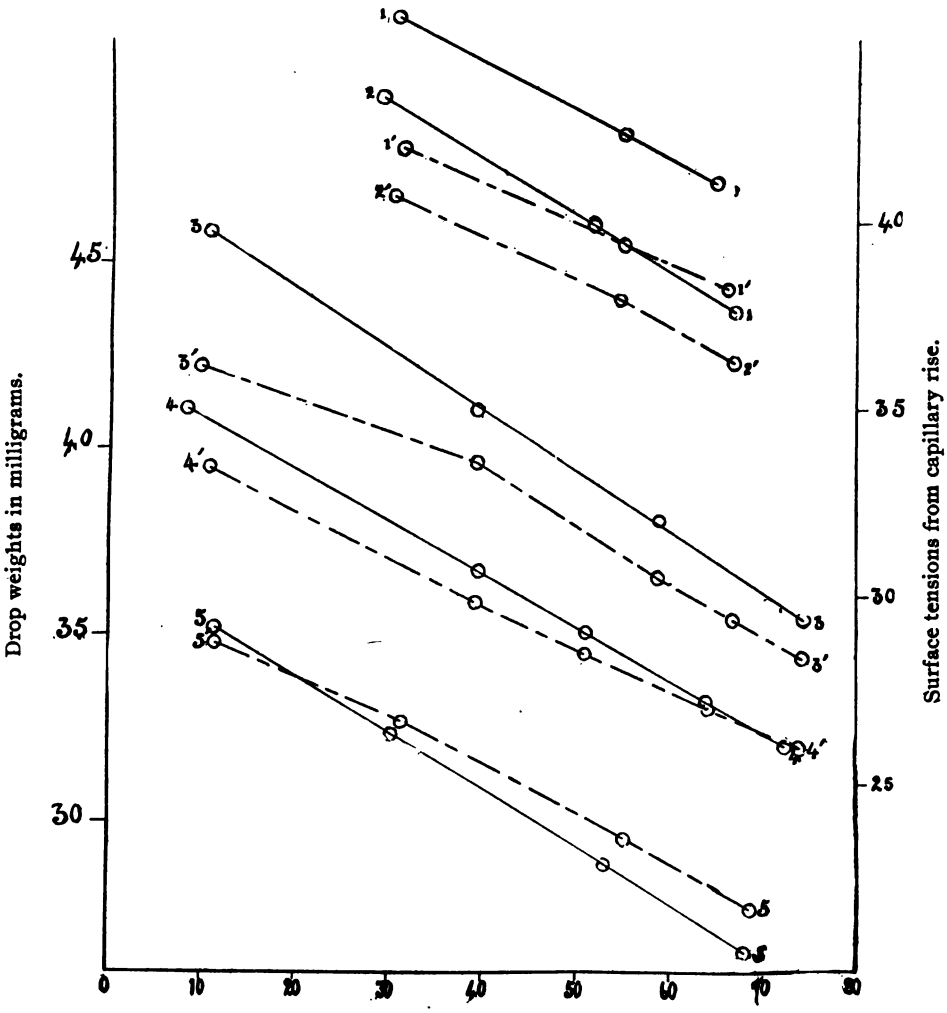


FIG. 4.

	Drop weight.	Capillary rise.
Quinolene	1	1′
Aniline	2	2′
Pyridene	3	3′
Chlorbenzene	4	4′
Benzene	5	5′

TABLE I.—*Continued.*

Temp.	Drop volume, cc.	Mean volume, cc.	Density.	Drop weight, mmg.	$K_{temp.}$	$k_{R\ \&\ G.}$
53.0	0.034201 0.034210 0.034191 0.034202	0.034201 ±0.000.004 or 0.01%	0.844	26.866	2.606	2.380
68.5	0.032076 0.032090 00.032081 0.032074	0.03208 ±0.000.004 or 0.01%	0.827	26.530		

TABLE II.

CHLORBENZENE.

Temp.	Drop volume, cc.	Mean volume, cc.	Density.	Drop weight, mmg.	$K_{temp.}$	$k_{R\ \&\ G.}$
8.2	0.036656 0.036700 0.036684	0.03668 ±0.000.013 or 0.04%	1.1200	41.082	2.568	2.332
39.2	0.033738 0.033729 0.033746 0.033746	0.03374 ±0.000.007 or 0.02%	1.0856	36.628	2.590	2.118
50.8	0.032647 0.032600 0.032588	0.03261 ±0.000.019 or 0.06%	1.0730	34.990	2.545	2.045
63.9	0.031350 0.031300 0.031391 0.031359	0.03135 ±0.000.018 or 0.06%	1.0590	33.200	2.577	1.938
72.2	0.030540 0.030523 0.030540 0.030529	0.030533 ±0.000.004 or 0.01%	1.0498	32.054		

TABLE III.

CARBON TETRACHLORIDE.

Temp.	Drop volume.	Mean volume.	Density.	Drop weight.	$K_{temp.}$	$k_{R\&G.}$
24.2	0.019600	0.01958	1.5823	39.976		
	0.019564	±0.000.007				
	0.019577	or 0.04%			2.567	
54.0	0.017516					
	0.017505	0.017510	1.5240	26.685		
	0.017510	±0.000.003				
	0.017511	or 0.02%				

TABLE IV.

PYRIDENE.

Temp.	Drop volume.	Mean volume.	Density.	Drop weight.	$K_{temp.}$	$k_{R\&G.}$
10.5	0.046238					
	0.046194	0.04622	0.991	45.804		
	0.046228	±0.000.014				
		or 0.036%			2.580	1.57
39.2	0.042665					
	0.042630	0.04260	0.962	40.98		
	0.042585	±0.000.02				
	0.042570	or 0.05%				
	0.042550				2.440	2.54
58.8	0.040312					
	0.040343	0.040295	0.943	38.00		
	0.040348	±0.000.025				
	0.040238	or 0.06%				
	0.040234				2.770	2.31
74.2	0.038180	0.038154	0.927	35.37		
	0.038153	±0.000.01				
	0.038128	—or 0.025%				
	0.038154					

TABLE V.

ANILINE.

Temp.	Drop volume.	Mean volume.	Density.	Drop weight.	$K_{temp.}$	$k_{R\&G.}$
29.0	0.048720					
	0.048688	0.04869	1.0138	49.362	2.5685	
	0.048662	±0.000.017				
		or 0.03%				

TABLE V.—*Continued.*

Temp.	Drop volume.	Mean volume.	Density.	Drop weight.	$K_{temp.}$	k R&G.
51.7	0.046154 0.046159 0.046170 0.046161	0.046161 ±0.000.004 or 0.01%	0.9944	45.903	2.5700	
67.1	0.044436 0.044432 0.044428	0.044432 ±0.000.002 or 0.01%	0.9810	43.588		

TABLE VI.

QUINOLENE.

Temp.	Drop volume.	Mean volume	Density.	Drop weight.	$K_{temp.}$	k R&G.
30.7	0.047456 0.047504	0.04748 ±0.000.024 —or 0.05%	1.0852	51.525	2.580	
55.0	0.045338 0.045347 0.045405	0.045363 ±0.000.021 or 0.05%	1.0658	48.344	2.570	
65.0	0.044474 0.044478 0.044518	0.044490 ±0.000.014 —or 0.03%	1.0576	47.053		

Showing $K_{temp.}$ k and critical temperatures. Drop-weight results are from the directly observed values at the extreme temperatures, those from capillary rise being from the smoothed curves.

TABLE VII.

Liquid.	$k_{temp.}$	Crit. temp.	k R&G.	Crit. temp.	Observed crit. temp.
Benzene	2.569	288.4	2.12	287.7	ca 288
Chlorbenzene	2.569	359.5	2.10	357.7	ca 360
Carbon tetrachloride	2.567	285.2	2.19	278.0	ca 284
Pyridine	2.567	347.0	2.07	346.2	ca 344
Aniline	2.569	425.8	2.01	448.6	ca 426
Quinoline	2.575	520.4	2.21	496.2	<520
Average	2.5694+ 0.013 or 0.05%		2.116±0.0965 or 4.6%		

Mean error of a single result
±0.0033 or 0.13%

Discussion of Results.

A glance at Tables I–VI will show that only in one case is my error in the estimation of the volume of a single falling drop, assuming the existence of no constant error, equal to 0.07 per cent., all others being very much less. Drop weights, calculated from these volumes and the carefully redetermined densities, can then of course, be burdened with no greater error. From the curves in Figure 4, where drop weights in milligrams and surface tensions from capillary rise in dynes are plotted against temperatures, it will be seen that the results of drop-weights are more concordant among themselves, than are the surface tension values, which allows of but one conclusion—the drop-weight method is more accurate than that based on capillary rise, even in the hands of such skilful investigators as Rénard and Guye. If there is then any doubt as to the drop-weight method giving the TRUE relative values of surface tension, rather than the method of capillary rise, one need simply turn to Table VII, in which $K_{temp.}$ for the six non-associated liquids used, is shown to be 2.5694 ± 0.05 per cent., the mean error of a single result being 0.13 per cent., while the variation in the corresponding average k value by capillary rise is 4.6 per cent. from Rénard and Guye's results, and much larger according to those of Ramsay and Shields'. When it is remembered that the Ramsay and Shields formula from which $K_{temp.}$ and k are derived, which may be written in the form

$$\frac{x_1\left(\frac{M}{d_1}\right)^{\frac{2}{3}} - x_2\left(\frac{M}{d_2}\right)^{\frac{2}{3}}}{T_2 - T_1} = \text{constant}$$

where x is a term proportional to surface tension, was originally designed for capillary rise results, it is quite evident that drop weight is not only also proportional to TRUE surface tension, but gives better and more consistent values for it than capillary rise. The same reasoning holds also with regard to the critical temperatures, and the Ramsay and Shields formula from which they are calculated except

that here the comparison cannot be made quite so satisfactorily, owing to necessary experimental uncertainty in the determination of critical temperatures. Even here, however, the drop-weight method shows to advantage, for the critical temperatures calculated by it for aniline and quinoline agree well with the experimental values, where those by aid of capillary rise are quite different. Drop weights, then, satisfy the equations that were designed especially for capillary rise results better than these themselves do.

This form of proof of the advantage in accuracy of the drop method over that depending upon capillary rise is, unfortunately, the only one possible at present, for even a smoothed curve drawn from the capillary rise results is still too much burdened with error to allow any very accurate, direct comparison of the two methods.

Owing to the unsatisfactory nature of the curve for the surface tensions from capillary rise, I have omitted any attempt to calculate the single values of the Morgan and Stevenson term $k_{F.D.}$, for the different liquids and temperatures, but have calculated for the sake of comparison, for I have made no other use of it, one single value of it in the following way: Since $K_{temp.}$ and k are related to each other as the drop weights are to the surface tensions, the ratio $K_{temp.}\ k$ must give the factor by which drop weights in milligrams must be divided to give TRUE surface tensions in dynes per centimeter. This factor is *1.2144* since $K_{temp.}$ is equal to 2.5694 and practically invariable, and the mean supposedly correct value of $k_{R.\&G.}$ is 2.116.

With the exception of aniline and quinoline drop weights interpolated (or extrapolated) from my curve agree with those found with the same tip by Morgan and Stevenson within a few tenths of one per cent. With aniline and quinoline the difference is slightly larger, but all are well within the limits of error mentioned in their paper. These slight errors, unavoidable at that time with their densities, however, are sufficient to account for the slightly larger value of $K_{temp.}$ and its variation which they observed, *i. e.*,

the value 2.598 ± 1.56 per cent. as compared to 2.5694 ± 0.05 per cent., and also for the difference in $K_{F.D.}$ which in average they found to be 1.226 as against my value of 1.2144. And the same is true for their critical temperatures.

Certainly the most striking and important fact brought out by my work is the practically absolute constancy for all the liquids at all the temperatures of the molecular temperature coefficient of drop weight, $K_{temp.}$ for it apparently makes the drop-weight method for large temperature intervals, where slight errors in temperatures have little effect, the most accurate known method for the determination of molecular weight, with the exception of that for permanent gases which is based upon the density. The truth of this can be shown by assuming as correct either the maximum, minimum or the average value of $K_{temp.}$ in Table VII, and calculating from it by aid of the specific drop weights and densities the molecular weight of any of the liquids given, the maximum error for any of the six liquids being less than 0.05 per cent. when M for the liquid giving the smallest value of $K_{temp.}$ is calculated from the largest value found for $K_{temp.}$ and is very much less when the M for any liquid is calculated from the average $K_{temp.}$ for it can be readily shown that the percentage variation in M is equal to 3/2 the percentage variation in the $K_{temp.}$ used for the calculation.

Another advantage of the constant value of $K_{temp.}$ is that it is not necessary for the calculation of the critical temperature from drop weight, as Ramsay and Shields found it in using the capillary rise values to first find the exact value of the coefficient for the specific liquid in question, for I can simply use the value of $K_{temp.}$ as found for any other non-associated liquid.

Summary.

1. An apparatus is described by which, using the same tip employed by Morgan and Stevenson, the error (assuming the existence of no constant error) in the estimation of the volume (and consequently of the weight) of a single falling

drop is reduced to a few hundredths of one per cent.

2. The elimination of their known error and a redetermination of the densities confirm all the conclusions of Morgan and Stevenson, as regards any one beveled tip, the more accurate work simply accentuating them and proving the drop-weight method to be even better than they claimed.

3. Drop weights calculated from the experimentally observed volumes by the aid of redetermined densities for benzene, chlorbenzene, carbon tetrachloride, pyridene, aniline and quinolene, at the same or nearly the same temperatures at which the surface tensions from capillary rise have been measured, show that drop weights are proportional to the temperature, and that the singly determined values lie upon a straight line, whereas the values from capillary rise vary considerably and irregularly, on the one side or the other of such a line. In other words, drop weight leads more accurately to the TRUE surface tensions than does capillary rise.

4. The molecular temperature coefficient of drop weight calculated by aid of the Ramsay and Shields formula

$$\frac{x_1\left(\frac{M}{d_1}\right)^{\frac{2}{3}} - x_2\left(\frac{M}{d_2}\right)^{\frac{2}{3}}}{T_2 - T_1} = \text{constant},$$

where x is a term proportional to surface tension, which was designed especially for results from capillary rise, is found for the drop weight to be practically invariable for all the six non-associated liquids, while the use of capillary rise leads to a variation of 6.4 per cent. from the average according to the results of Rénard and Guye, and to a still larger one, according to those of Ramsay and Shields. The consequence of this is that the drop-weight method when used for such a temperature interval as I have employed is the most accurate method for the determination of molecular weight known, with the exception of that for permanent gases as based upon the density. And critical temperatures can be more

readily and accurately calculated from drop weight than from capillary rise, as is shown for aniline and quinolene by he agreement with experiment when calculated drop weight and the wide divergence when calculated from capillary rise.

Second Part.

On Some New Formulae Relating the Various Constants for Non-Associated Liquids.

It was shown by W. G. Kistiakowsky[1] that the relation

$$\frac{AM}{T} = K_k$$

holds for a large number of substances where M = molecular weight in liquid state, A = capillary constant (rise in a capillary tube of unit radius), and T = absolute boiling-point, the value of K_k varying from 1.04 to 1.17.

It has been shown that the drop weight of non-associated bodies is proportional to the surface tension, hence by the equations

$$\gamma = \frac{1}{2} grhd \text{ and } w = vd.$$

It is obvious that by substituting b for "A" in the Kistiakowsky relation I should obtain a constant similar to that obtained from the capillary constant provided the volume be that delivered from unit tip. Since I have insufficient data to enable me to calculate the magnitude of v under those conditions, I must employ the drop volume obtained in the preceding work. This will not affect the constancy of the relation but will simply lead to a new empirical constant.

$$\frac{vM}{T} = K.$$

Solving for the extrapolated values for drop volume the following results are obtained:

[1] Zeit. f. Elektrochem. (8) 375, 1902 and (12), 513, 615, 1906.

TABLE I.

Substance.	K.
Benzene	67.4
Pyridene	67.3
Chlorbenzene	68.4
Aniline	67.6
Quinolene	68.8

Showing the statement to be as generally justifiable for drop volume as for capillary rise despite the extrapolation in the first case since drop volumes have not been estimated up to the boiling-point. In any subsequent use of drop-volume determination as a method for obtaining molecular weights, it would be advantageous if such a formula as the above could be shown to be general at temperatures other than the boiling-point, since the molecular weight of a non-associated body could then be calculated from a single estimation at a temperature which would introduce no extra experimental difficulties. The most probable direction for the formula to take is that of "corresponding states" shown to be at least approximately true by the following results:

TABLE II.

Substance.	Mean specific temperature coefficient of drop volume.	Mean molecular co-efficient.
Benzene	13315	0.0104
Pyridene	12669	0.0100
Chlorbenzene	09605	0.0108
Quinolene	08717	0.0103
Aniline	11175	0.0104
Carbon tetrachloride	06946	0.0107
		0.01043±4%

An agreement closer than that of k (Ramsay and Shields) by the capillary rise method and derived direct from experimental results not from a smoothed curve. It thus seems probable that the formula

$$\frac{Mv}{T} = K_{(BT-T)}$$

will be found to hold at all corresponding temperatures where M = molecular weight, v = drop volume, T = absolute temperature of observation. $K_{(BP-T)}$ = constant for the particular state, *i. e.*, for the difference between the temperature of estimation and the boiling-point. Solving the equation for the formerly obtained experimental values we obtain by extrapolation the numbers shown in Table III.

The agreement is very good, considering that the values are nearly all from extrapolated drop volumes, some, as with aniline and quinoline over more than 100° C. The deviations from the average are apparently no function of the molecular weight or boiling-point, and are consequently probably due largely to errors of extrapolation. The generalization is, however, likely only to be accurate at temperatures not too far removed from the boiling-point as evidenced by the increase of percentage variation in the values for K as we retreat from the boiling-point and by the fact that if it held rigidly very far above the boiling-point it would force the conclusion that the critical temperature of all non-associated bodies lay at the same distance from their boiling-point, a conclusion contrary to fact.

Further work may make it possible to correct the formula much as Trouton's law has been modified by Nernst, but for the present approximate accuracy only is attainable. It now remains to show what may be derived from the formula in its present state.

1. Use of the formula to derive molecular weight from a single drop-volume determination.

The values used for K are those obtained by averaging the numbers shown in Table III, eliminating the values for quinolene and aniline at temperatures less than 80° from the boiling-point so that all experimental values for K are extrapolated over the same range.

The drop volumes used are those directly obtained, no attempt being made at mutual correction, so that the values are such as would be obtained from isolated determinations.

TABLE III.

Substance.	Values of K for temperatnre below the boiling-point of: 0.	10.	20.	30.	40.	50.	60.	70.	80.	90.	100
Benzene	6736	7232	7763	8331	8925	9553	10200	10960	..	..	..
Pyridene	6727	7178	7640	8141	8493	9213	9808	10430	1110	1180	1256
Aniline	6765	7159	7575	8007	8460	8936	9437	9969	1052	1111	1173
Chlorbenzene	6844	7302	7777	8284	8807	9365	9963	10580	1124	1185	1270
Quinolene	..	..	..	8593	9006	9413	9914	10390	1090	1139	1198
	6768	7218	7689	8269	8738	9296	9864	1046	1094	1154	1224

TABLE IV.

Substance.	Boiling-point.	Molecular weight.	Calculated molecular weight from experiments over range of 10° to 60° C.	
Chlorbenzene.....	132	112.4	111.8	—112.2
Pyridene	114.5	78.0	79.0	— 80.0
Aniline.....	183.5	93.0	100.0	—101.0
Benzene.....	80.4	79.0	79.0	— 80.0

This gives from estimations burdened with ordinary experimental error as close agreement as necessary for practical work in the laboratory, even assuming the average values of K used to be accurate, which is scarcely probable. The formula has thus sufficient accuracy in its present form for use in the organic laboratory.

$$\text{If } \frac{Mv}{T} = K_{(BP-T)}$$

is generally true in the neighborhood of the boiling-point, it follows that

$$v = \frac{K_{(BP-T)}T}{M} \text{ and } w = \frac{TK_{(BP-T)}}{M}d;$$

hence, if the molecular weight of a body be known the value of the drop volume can be calculated by use of the various values of K and by using the corresponding value for density we can write the formula of Ramsay and Shields:

$$\frac{K_{(BP-T)}T}{M}d\left(\frac{M}{d}\right)^{\frac{2}{3}} = K_{temp.}(\tau - 6)$$

and thus calculate the critical temperature as shown in Table V.

TABLE V.

Substance.	Molecular weight.	Boiling-point.	Critical temperature from $K_{(B.P.-\infty)} = 766$.	Average critical temperature from $K_{B.P.}$ to $K_{B.P.-40}$.	Mean experimental values.
*Chloroform.....	119.4	61.2	262.4	263.0	260±
Chlorbenzole.....	112.4	132.0	356.5	359.1	360±
*Ethylidene chloride..	98.9	59.2	255.7	256.0	255±
*Toluene.....	92.0	111.0	320.1	320.6	321±
Pyridene	79.0	114.5	347.75	348.3	345±

The density data for the 3 bodies marked* were obtained from smoothed curves from values published in Beilstein and elsewhere.

The agreement is good, especially that obtained by averaging the values over a series of K's indicating the error largely to lie in their insufficient definition. It is also interesting to note that ethylidine chloride, toluene and chloroform give correct results using as $K_{temp.}$ the value established as a constant in previous work with other bodies, *viz.*, 2.569.

Expressing in formula form these results become

$$(1) \qquad M = \frac{TK_{(BP-T)}}{v} \text{ or } v = \frac{TK_{(BP-T)}}{M};$$

$$(2) \quad vd\left\{\frac{K_{(BP-T)}T}{vd}\right\}^{\frac{1}{3}} = K_{(temp.)}(\tau - 6) = (vd)^{\frac{1}{3}}(K_{(BP-T)}T)^{\frac{1}{3}};$$

$$(3) \quad \frac{K_{(BP-T)}Td}{M}\left(\frac{M}{d}\right)^{\frac{1}{3}} = K_{temp.}(\tau - 6) = K_{(BP-T)}T\left(\frac{d}{M}\right)^{\frac{1}{3}}.$$

Where v = drop volume, d = density } at temperature T (absolute)

M = molecular weight τ = critical temperature — T $K_{(B.P.-T)}$ constant for condition at boiling-point — T degrees below boiling-point.

Since it has been shown that the critical temperature of a body can be calculated from a knowledge of its boiling-point, molecular weight, and a single density with an accuracy equal to that obtainable by direct experimental determination, it follows that we might by substitution of such a derived critical constant in the Nernst[2] modification of Van der Waals' equation, 1, using the boiling-point as the specific state, solve for the critical pressure:[3]

$$\log \frac{\pi}{p} = 1.75 \log \frac{T_c}{T} + \alpha^1\left[\left(\frac{T_c}{T} - 1\right) - \frac{1}{2.36}\left(1 - \frac{T}{T_c}\right)\right]$$

p, thus becoming unity and T the boiling-point of the sub-

stance, T_c being the critical temperature, solved by equation 3.

π being thus obtained, substitution of any other value for T in Nernst's equation leads to the evaluation of p (the vapor pressure) at any temperature.

With π (critical pressure) and T_c thus obtained the values of "a" and "b" in Van der Waals' gas equation are determinable

$$a = \frac{27}{64\ 273^2}\frac{T_c^3}{\pi}$$

$$b = \frac{1}{8\ 273}\frac{T_c}{\pi}$$

and still again knowing the value of π and p we may obtain the latent heat of vaporization from Nernst's[1,2] modification of Trouton's law.

$$\frac{\lambda}{1-\frac{p}{\pi}} = R\frac{T_1T_2}{T_1-T_2}ln\frac{p_1}{p_2}.$$

Summing up, therefore, I find that for a number of unassociated liquids:

(*a*) From a knowledge of the boiling-point of the liquid and its molecular weight and a density we can by use of drop-volume constants determine with very fair approximation:

1. The surface tension (in terms of drop weight).
2. The critical temperature and pressure, and hence,
3. The vapor pressure at any temperature.
4. The latent heat of evaporation.

[1] Nachrichten Kgl. Ges. Wiss. Göttingen, 1906.

[2] J. A. C. S., "Bingham," June, 1906.

[3] Van der Waals' "Die continuität des Gasförmigen und Flussigen Zustandes," pp. 166–167.

"Ist der Radius der Attraction bei allen Körperm gleich gross, so muss Capillaritätsconstante fur die verschiedenen Körper dem kritischen Druck proportional sein."

5. The value of "a" and "b" in the Van der Waals' equation for the particular body.

(b) From a drop-weight determination, by the same constants and a knowledge of the boiling-point we can calculate the molecular weight of a body and hence all the values under (a).

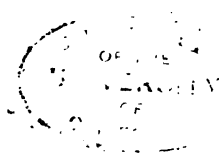
As to how far the equations in an unmodified form are absolutely general, insufficient data has yet been accumulated to show, nor have the values of K been defined with sufficient accuracy.

Further work must be done upon this subject and on formulae and relations derivable from it, the present being more in the nature of a note than any attempt at a full treatment.

With approximate accuracy the values for K are:

$K_{(B.P.)} = 660$ $K_{(B.P.-20)} = 766$ $K_{(B.P.-40)} = 880$
$K_{(B.P.-10)} = 713$ $K_{(B.P.-30)} = 824$ $K_{(Temp.)} = 2.569$

LABORATORY OF PHYSICAL CHEMISTRY,
COLUMBIA UNIVERSITY,
April, 1908.



BIOGRAPHY.

Eric Berkeley Higgins was born August 12, 1885, in Sunderland, Durham, England. He graduated from the Technical Institute, Manchester, in 1903, and Victoria University, Manchester, in 1906. Since that time he has been in the employ of Messrs. Crosfield, Son & Company, of Warrington, England, from whom he has obtained leave of absence to complete his graduate work for the Ph.D. degree at Columbia University.

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